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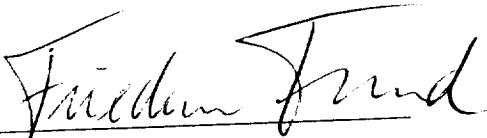
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Cooperative Agreement
NCC 2-572

Mineralogical Investigation of a Variety of Materials Using Analytical Electron Microscopy (AEM)

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Summary

Understanding the origins of Life requires a good understanding of the physics and chemistry of biogenic low-z elements H, C, N, O, P, S in terrestrial environments, on Mars, on extra-terrestrial bodies such as meteorite parent bodies and comets, and in interstellar space. Under this Cooperative Agreement six tasks have formed a coherent program aimed at elucidating various aspects of low-z element geo- and cosmochemistry with special reference to the origin of Life on Earth and to the search for life on Mars.

- Task (1) Formation of organic molecules or precursors thereof of the composition $H_xC_yO_z^n$, inside the hard matrix of structurally dense magmatic minerals;
- Task (2) Formation of organic molecules inside the soft matrix of amorphous and crystalline water ice and their preservation in interstellar and planetary ices.
- Task (3) Preservation of organic molecules in cherts and other siliceous rocks formed in hot spring or submarine hydrothermal vent environments;
- Task (4) Nature of the elusive Martian soil oxidant and development of the Charge Distribution Analysis (CDA) technique for potential use in landed missions.
- Task (5) Prototype development of an XRD instrument, using an XRD camera with a Charge Coupled Device (CCD) as camera and as energy-dispersive analyzer.
- Task (6) Analysis of stratospheric aerosols and characterization of soot and sulfuric acid aerosols collected by NASA's highflying aircraft

Task 1 describes a series of experiments to identify solute carbon as an "impurity" in the structure of minerals grown or recrystallized in CO/CO₂-laden environments. The presence of solute carbon has been inferred from peroxy radicals which derive from a particular redox reaction within the mineral structure which, in the case of solute H₂O, is already well understood. The presence of simple organics with a ¹³C signature in the minerals indicates the redox reaction involving solute CO/CO₂. Organic molecules by such a mechanism may have provided a source of abiogenically formed organic matter on the early Earth.

Task 2 describes the synthesis and characterization of water ices which are analogs to extraterrestrial ices found within comets and cold molecular clouds. Under this Task an existing electron microscope was modified to allow for the low-temperature vapor deposition, processing and analysis of ices. Ice samples were studied during warm-up from 12 K to 300 K. Structural

and morphological changes occurring during volatilization, crystallization and phase changes were monitored as a function of temperature. The structure of the ice has been characterized by electron diffraction. The results are used to model the phase transformations which occur within comets as they enter the inner solar system, and within cold molecular clouds heated by embedded stars.

Task 3 involves the selection and evaluation of landing sites of exobiology interest on Mars and studies of Mars analog landing sites on the Earth. Thermal spring environments are regarded as important environments for early life on Earth. Modern and ancient hot spring sites on Earth will be evaluated as to their potential to harbor and preserve fossil evidence of life. Ancient hot spring deposits on Mars may hold an opportunity for preserving fossil evidence of early Martian life, if ever it developed there. Studies of fossilization processes in thermal spring environments will be conducted. They are important for understanding how biological information is retained in thermal spring deposits, and how variations in temperature or other parameters influence styles of preservation. This information is not only prerequisite for understanding the ancient record on Earth, but also provides information needed to formulate meaningful strategies for the exploration of Mars.

Task 4 describes a physical technique, Charge Distribution Analysis or CDA, which has been developed to study the effects of peroxy defects in mineral matrices. These peroxy entities represent the oxidized portion of the redox reaction mentioned under Task 1. Under UV irradiation they give rise to highly oxidizing surface radicals which may be the essence of the Martian soil oxidant. A benchtop CDA instrument has been built.

Task 5 describes the fabrication of a breadboard instrument which simultaneously detects diffracted and fluoresced X-rays. A compact, low-power XRD/XRF was designed, incorporating a CCD (Charge Coupled Device) imaging device in place of the film cassette, to be used in planetary missions. The SETI portion of the project involves evaluating the design of the device and fabricating a prototype system using an X-ray CCD array imaging detector. A patent was submitted last year. Research will be conducted into the geometry of the device and the evaluation of a specific CCD array will be undertaken.

Task 6 describes the analysis of Stratospheric aerosols and the evaluation of the potential for these particles to act as catalytic surfaces for heterogeneous chemistry. The chlorofluorocarbon (CFC) induced reduction of ozone in the Antarctic stratosphere and radiative cooling of the global atmosphere due to sulfate aerosols from the eruption of Mt. Pinatubo emphasize the need for anthropogenic and natural influences. It has been discovered that chemical reactions taking place on aerosol particles activate chlorine, making it available to catalytically destroy ozone. The research conducted under this Task is directed towards the characterization of airborne soot and sulfuric acid aerosols, and to the study of the potential of these aerosols to absorb nitrogen and the halides.

Description of the Results Obtained within each Task

Task 1. Formation of Organic Matter from Carbon Dissolved in Minerals

Before Life could start on Earth, there must have been a large reservoir of prebiotically formed organic matter. Basic research into the origin of Life has been based on the premise that those relatively simple organic molecules that act as building blocks for more complex, biochemically relevant molecules must have formed either during highly energetic processes on Earth involving electric discharges, UV irradiation, etc., or in outer space. However, the synthesis of the complex molecules from simple building blocks still remains problematic.

The possibility cannot be ruled out that a fundamentally different mechanism may exist for the synthesis of organic molecules which could profoundly change our understanding of the earliest prebiotic reservoir from which Life arose. Indeed, there are strong indications that such a mechanism exists. We have shown that simple oxide crystals grown from a melt under reducing conditions, in a CO/CO₂/H₂O atmosphere, and cooled to room temperature, contain oxygen in an oxidized form as peroxy or O⁻. The presence of O⁻ is a thermodynamic paradox since O⁻ is an indicator of highly oxidizing growth conditions. The paradox is resolved by an internal conversion which oxidizes lattice oxygen from its regular -2 oxidation state to the -1 oxidation state. Such a conversion must be balanced by a redox reaction in the course of which something else is reduced.

This "something" is hydrogen: OH⁻ impurities which derive from traces of lattice-dissolved H₂O convert to H₂ + 2 O⁻. The conversion occurs reversibly at moderate temperatures (<500°C) and is driven by the slight departure from thermodynamic equilibrium achieved during cooling of crystals from higher temperatures. We have measured the formation of H₂ by infrared and mass spectroscopic techniques and ascertained the formation of peroxy and O⁻ by magnetic, dielectric and chemical titration techniques. Since the crystals in which the 2OH⁻ ⇒ H₂ + 2O⁻ conversion occurred had been grown in a CO₂-rich atmosphere, traces of CO₂ are co-dissolved along with H₂O. The solutes CO and CO₂ are subject to the same redox conversion, splitting into oxidized O⁻ plus reduced C. In this case, H₂ molecules and reduced C will be present in the same crystal matrix. The next step is that, when H₂ and C co-exist in a crystal, they both segregate during cooling to 1- and 2-dimensional defects such as dislocation lines and subgrain boundaries. At such defects they form H-C-O⁻ and C-C-O⁻ bonds. When hydrolyzed during dissolution, these lattice-bound precursors turn into organic molecules of the general formula C_xH_yO_z.

Single crystals of MgO and olivine have been crushed and extracted with organic solvents of increasing polarity: first chloroform, acetone, tetrahydrofuran (THF), and with H₂O. Full procedural blanks were performed. IR spectra were recorded of the THF extracts from the MgO and olivine samples as well as those of the procedural blank with an empty thimble and of the residue of 250 ml THF as used for the extraction. The procedural blanks and the THF residue indicate that contamination is negligible. The MgO extract spectrum suggests the presence of H-

bonded -COOH and carbonyl groups of saturated aliphatic carboxylic acid dimers. A strong VCH band at 2870–2950 cm^{-1} , and a number of partly overlapping, unresolved bands appear in the 600–1500 cm^{-1} fingerprint region. The THF extract of olivine suggests the presence of H-bonded -COOH and carbonyl groups of saturated aliphatic carboxylic acid dimers, with additional bands in the 600–1500 cm^{-1} region and a sharp band at 1600 cm^{-1} .

The THF extract of MgO was redissolved in chloroform. Upon slow evaporation of the solvent, colorless crystals precipitated. Their melting point was 189–190°C, close to the 188°C reported for succinic acid. The IR spectrum of the crystals in a KBr pellet is shown in Figure 1c. The IR bands are characteristic of succinic acid. The mass spectrum (direct insertion probe) yielded an ion at m/z 119 along with fragments at m/z 73 and m/z 101. The m/z 119 peak is interpreted as the $(M+1)^+$ ion with the m/z 73 and 101 peaks indicating the loss of a carboxylic group, -COOH, and hydroxyl group, -OH, respectively, all consistent with succinic acid. The ^1H -NMR spectrum of the crystals redissolved in deuterated tetrahydrofuran (THF- d_8) shows a singlet at 2.54 ppm (with reference to tetramethyl-silane), arising from methylene groups, -CH₂-, and a broad, D₂O exchangeable singlet at 10.37 ppm, arising from carboxylic acid groups, -COOH, at an intensity ratio consistent with succinic acid. An x-ray structure analysis was performed, using a plate-like single crystal of about 100 μm . The monoclinic space group was determined to be P2₁/a with the unit cell dimensions $a_0 = 5.086$, $b_0 = 8.845$, $c_0 = 5.543$, with $\beta = 90.9^\circ$, close to the values reported for β -succinic acid, $a_0 = 5.126$, $b_0 = 8.880$, $c_0 = 5.519$, and $\beta = 91.3$, crystallized from an ethyl acetate solution.

Probable mass fragments	amu
CH ₂ =CH ⁺	27
CH ₃ -CH ₂ ⁺	29
CH ₂ =CH-CH ₂ ⁺	41
CH ₃ -CH ₂ -CH ₂ ⁺ or CH ₃ CO ⁺	43
CH ₂ =CH-CH ₂ -CH ₂ ⁺	55
CH ₃ -CH ₂ -CH ₂ -CH ₂ ⁺ or CH ₃ -CH ₂ CO ⁺	57
CH ₂ =CH-CH ₂ -CH ₂ -CH ₂ ⁺	69
CH ₃ -CH ₂ -CH ₂ -CH ₂ -O ⁺ or CH ₃ -CH ₂ COO ⁺	73
CH ₂ =CH-CH ₂ -CH ₂ -CH ₂ -CH ₂ ⁺	83
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -O ⁺ or CH ₃ -CH ₂ -CH ₂ COO ⁺	87
CH ₂ =CH-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ ⁺	97
CH ₂ =CH-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ ⁺	111
CH ₂ =CH-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ ⁺	125
CH ₂ =CH-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ ⁺	139
CH ₂ =CH-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ ⁺	153

Sequence of Longchain Hydrocarbons Extracted with Chloroform from Crushed Upper Mantle-Derived Olivine Single Crystals and Analyzed by GC-MS [Gas Chromatography-Mass Spectroscopy; amu: atomic mass units]

By extracting crushed olivine from the upper mantle, even C-rich organic molecules were obtained. Compounds tentatively identified in the chloroform extract are given in this table.

This work shows that organic molecules of surprising complexity can be generated inside the dense matrix of crystals like MgO. The solid state processes by which these delicate molecules, or precursors thereof, form are well understood, though much work is still needed to determine how much of the total carbon contained in the MgO crystals turns into organic matter. We also need to map out the complexity of the organic molecules and to relate them to the crystal structure from which they segregate. For instance, the long-chain aliphatic and olifinic molecules suggest that they derive from C-C backbones which segregated into dislocation lines. The dicarboxylic acids suggest that some of the C atoms remain bonded to lattice O while making C-C and C-H bonds.

Our findings have importance for the Exobiology and for the search of the origins of Life. The MgO crystals are a model and their study represents only the first step in a multiyear project aimed at extending our study to natural minerals. The MgO crystals have already helped us greatly to decipher the fundamental processes that lead to the formation of complex organic molecules by segregation in the solid state. Similar processes are expected to take place in rocks which solidify from magmas saturated with the common volcanic gases CO₂ and H₂O. When the rocks cool, carbon and hydrogen within their constituent minerals can be expected to segregate to internal defects. When the rocks are exposed at the surface of the Earth, due to volcanic or tectonic forces, their minerals disintegrate through weathering. During disintegration they will release whatever carbon-carbon and carbon-hydrogen entities they contain, thus releasing rock-made organics into the surface environment. We thus arrive at the fascinating prospect that magmatic rocks from the depth of the Earth may be carriers of complex organic molecules. If this is true, rock-made organic matter may have played a role during the early history of the Earth when Life arose.

Publications from Task 2:

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F. Freund, A. Gupta, and D. Kumar, Organic matter from H₂O and CO₂ dissolved in minerals, Lunar and Planetary Science Conference, (Houston: Lunar Planetary Institute, 1996) 27: 379-380.

F. Freund, and R. Ho, "Organic matter supplied to a planet by tectonic and volcanic activity," Circumstellar Habitable Zones, Ed. L. R. Doyle (Menlo Park, CA: Travis House Publ., 1996) 71-98.

Task 2. Ultrastructural and Microchemical Investigation of Extraterrestrial Ice Analogs.

In this work, a modified Analytical Electron Microscope is used which allows for the low-temperature deposition, processing and analysis of ices formed by vapor deposition. As amorphous ice samples are warmed from 12 K to 300 K, a series of changes occur including outgassing, sublimation, crystallization, changes in amorphous form, restructuring into clathrates, and transition through the glass temperature. The changes are monitored as a function of temperature. During warming, the sample is viewed at high resolution and as phase changes are perceived, diffraction patterns and images are recorded. A quadrupole mass spectrometer is used to monitor gas release as a function of temperature.

Vapor deposited amorphous water ice plays an important role in astrophysics. Solid ice is observed as a frost on interstellar dust in dense molecular clouds, it constitutes the bulk of matter in comets, and is found on the surfaces of planets and their satellites. Our work is designed to help interpret the dynamical processes that underlie the formation of organic matter, observed in laboratory experiments that simulate interstellar ices, and interpret the complex outgassing phenomena observed in laboratory analogs of cometary ices. Vapor deposited ice at low pressure has four known structures. These are, in order of the temperature regime at which they are formed: A high density amorphous form I_{ah}, a low density amorphous form I_{al}, a cubic crystalline phase I_c, and an hexagonal crystalline phase I_h.

We have made a number of discoveries using our modified TEM: Jenniskens and Blake (1994) were finally able to confirm the existence of the high-density vapor deposited form reported by Narten et al. (1976). Jenniskens et al. (1995) further studied the deposition conditions necessary for the creation of this form, the expected time dependence, and performed molecular dynamics calculations to simulate the high-density ice structure. Jenniskens and Blake (1996) investigated the crystallization behaviour of water and discovered that the crystallization rates imply that the liquid form of water found just above the glass transition is a "strong liquid". This is the first direct evidence that this liquid form of water differs markedly from normal liquid water at high temperature, which is "fragile". Jenniskens and Blake (1996) discussed the interesting implications of the strong/liquid character of the ice for the crystallization behaviour of both pure and impure ices in the solar system.

Jenniskens et al. (1997), now accepted for publication in J. Chem. Phys., concludes that the strong liquid persists into the cubic regime. The first indication of this was given by the discovery that an amorphous component is always present in the diffraction patterns of ice films in the cubic regime, even when crystallization has completely stopped. The presence of this liquid form in such a broad range of temperature (150-200K, or a similarly wide range but at lower temperature on longer timescales) implies that this form is abundantly present in nature, where it is expected to occur in the subsurface layers of comets and the surfaces of planets and their satellites.

Publications from Task 2:

Wilson, M., A. Pohorille, P. Jenniskens, D.F. Blake, 1995, Probing the structure of cometary ice, *Origins of Life and Evolution of the Biosphere* 25, 3-19.

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Jenniskens P., Blake D.F., 1996, A mechanism for forming deep cracks in comets, *Planet. Space Sci.*, Vol 44, No. 7 pp 711-713.

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Jenniskens P., Blake D.F., 1996, Crystallization of amorphous water ice in the solar system, *The Astrophysical Journal* 473 (December issue in press).

Jenniskens P., Banham S.F., Blake D.F., McCoustra M.R.S., 1997, *J. Chem. Phys.* (accepted).

Task (3) Preservation of organic molecules in cherts and other siliceous rocks.

Studies of Modern and Ancient Thermal Springs To date, there have been very few reports, and essentially no detailed paleontological studies of early thermal spring settings on Earth, despite the fact that such studies provide the only direct record of evolution in those environments. In order to create a framework for recognizing thermal spring deposits in the ancient rock record, we have been carrying out studies of modern thermal spring systems in Yellowstone National Park, along with similar ancient deposits from localities in Western North America and Australia.

A primary goal of this research is to develop integrated paleobiological, sedimentological and geochemical models can be used to explore for ancient hydrothermal deposits on the Earth, and eventually on Mars. In our studies of ancient thermal spring deposits we seek a better understanding of how diagenesis, the changes in texture and composition that occur following burial, affect the long term preservation of paleobiological information.

In collaboration with Dr Sherry Cady (Ames NRC Fellow), studies of modern thermal springs lead to several new discoveries during the period of the grant that have helped refine our understanding of stromatolite morphogenesis and fossilization processes at high temperatures. Geysers, the highest temperature deposits of siliceous thermal springs, were first studied in the late 1970's and determined to be abiogenic. Since that time, many authors have questioned the biogenicity of the oldest fossil stromatolites suggesting that they were formed inorganically. But, our studies of modern geysers have revealed conclusively that these deposits actually form in the presence of thin biofilms of thermophilic archaeobacteria, and that microstructure reflects a significant biogenic contribution.

With collaborator, Dr. Malcolm Walter (Macquarie University, Sydney, Australia), we carried out a detailed study of ancient subaerial thermal spring deposits in NE Queensland, Australia. These deposits are precise analogs for subaerial systems we have been studying in Yellowstone, but are some 350 million years in age. In that study we observed that primary biofabrics are preserved despite extensive textural reorganization during diagenesis. This work was published in the journal *Palaos*, which describes the sedimentologic framework microbial microfabrics of the Queensland sinters. We are presently studying microbial stromatolites associated with one billion year old thermal spring deposits from central Montana. But the real excitement still lies ahead as we continue to follow the "trail" of thermal springs into the oldest geological terranes on Earth, including Archean sections in Western Australia, South Africa and Eastern Greenland.

Some additional accomplishments for the Thermal Spring Subtask are listed below:

- 1) In collaboration with Donald Lowe, completed field work and preliminary thin section studies of subsurface hydrothermal deposits at Gerlach, NV.

- 2) In collaboration with David Des Marais, completed preliminary isotopic analyses of active travertine springs at Mammoth Terrace, YSNP.
- 3) Mapped, sampled, thin sectioned and initiated petrographic study of Holocene-aged travertines at Gardiner, Montana for microfacies level comparisons with modern spring deposits at Mammoth Terrace, YSNP.
- 4) Published a work with Dave Des Marais describing the control of microorganisms on the formation of sedimentary fabrics in modern travertine spring deposits, Mammoth Terrace, YSNP.
- 5) In collaboration with Dave Agresti and Thomas Wdowiak (University of Alabama), completed preliminary field and lab work to determine Mossbauer spectral features of iron thermal spring minerals in YSNP.

Site Selection Studies for Mars Exobiology An important aspect of NASA's plan for future missions to Mars focuses on the selection of sites to explore for evidence of ancient life. The Viking biology experiments provided no evidence for extant life on Mars and it is generally agreed today that the most promising approach in exploring for life on Mars, at least in surface environments, is in searching for a record of an ancient Martian biosphere. Because Mars was more Earth-like early in its history (denser atmosphere and abundant liquid water), during the same time that life emerged on Earth (3.0 - 4.0 Ga), it is possible that life arose there as well, becoming extinct in surface environments as Mars lost its atmosphere and began to refrigerate. Thus, future exploration of the Martian surface will focus on the search for evidence of an ancient biosphere. Based on studies of the ancient fossil record on Earth, the most favorable places to search for a fossil record on Mars are geological settings where aqueous minerals are likely to have precipitated under biologically-favorable conditions. Candidate mineral deposits include deposits of subaerial thermal springs and or collar subaqueous spring deposits, evaporites, and mineralized subsoils where "hardpans" may have formed. On Earth, such deposits often contain well-preserved microbial fossils, and/or biomolecular compounds of great interest for Mars "exopaleontology".

High resolution visible range imaging is presently needed to accurately identify small-scale geomorphic features of the Martian surface. Such data will greatly improve present geological interpretations at high priority sites. Although elemental data were obtained for soils at the two Viking lander sites, we have yet to determine the mineralogical composition of the surface. Mineralogical data are crucial for selecting targets for future landed missions to search for a fossil record. Fortunately, a new ten year program of Mars exploration will begin in 1996 with launches of the Mars Global Surveyor (orbital) and Mars Pathfinder (landed) missions. Infrared spectroscopy obtained during the Surveyor mission will be used to map the surface mineralogy of Mars. During the Surveyor mission, only a limited number of targets will be selected for high resolution imaging. Thus, an important activity for the Global Surveyor Program is the identification of high priority imaging targets for Mars exopaleontology. In collaboration with Ron

Greeley (Arizona State University) we completed an initial survey of high priority sites on Mars for future exopaleontological missions during the period of the grant. These site evaluations were published in NASA Reference Publication 1238 "Mars Landing Site Catalog. (Second Edition)", and updated in NASA Special Publication 530 "An Exobiological Strategy for Mars Exploration". High priority targets for high resolution orbital missions during the Mars '96 orbital mission were presented to the mission planning teams, and recommendations for the Mars Pathfinder (landed mission) were presented at LPSC and the Mars Pathfinder Workshop (see published abstracts). Based upon our recommendation, the area at the mouth of Ares Vallis outflow channel was selected based upon its exopaleontological potential. Most recently I have been studying the potential for hydrothermal systems on Mars, and have identified eight major geotectonic settings most likely to have hosted thermal springs. This work was published in 1996 as a Chapter in the book "Evolution of Hydrothermal Ecosystems on Earth (and Mars?)" edited by Gregory Bock and Jamie Goode (see publications).

In addition, Earth-based remote sensing studies are also needed to equip us to better identify key mineral deposits from orbit. These studies must be carried out at terrestrial sites that are good analogs for exploration targets on Mars. Such analog studies will allow us to specify the threshold spatial and spectral resolutions needed to identify key deposits from orbit, and help us to develop methods of image analysis in advance of receiving new imaging data from Mars in 1997. In collaboration with James Brass (Code SG), we completed initial field and lab work for a remote sensing analog study at Mono Lake aimed to map carbonate and evaporite deposits in the Mono Basin using a hyperspectral near-IR data set (AVIRIS) acquired by an overflight by JPL in 1994.

We have also been developing recommendations for technologies needed to support the exopaleontological exploration of Mars during the Mars Surveyor Program and have participated extensively in the field testing robotic technologies to support basic science goals for Exopaleontology. During the period of the grant, I headed science teams for field trials of the Marsokhod at Amboy Crater, in the Mojave Desert ('94) and at Kilauea, Hawaii (1996). I also headed the science team for a TROV experiment at Mono Lake aimed at developing integrated tools for telepresence. I prepared reports for all of these tests documenting the results of those field experiments that are presently in press or being finalized for publication.

Publications from Task 3:

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Task 4. Charge Distribution Analysis (CDA) Technique

Over twenty years ago the Viking Mission's Life Detection Experiments did not find life on the Red Planet, but demonstrated that the Martian soil is extraordinarily oxidizing. Oxygen gas (O_2) evolved when the soil was exposed to water vapor (H_2O), and carbon dioxide (CO_2) evolved upon adding an aqueous solution with organic nutrients, intended to stimulate the growth of Martian living organisms. These observations characterize the Mars Soil Oxidant – a reagent so strong that it might have wiped out traces of life on Mars. The physical and chemical nature of this powerful oxidant is still unknown.

How did the Mars Soil Oxidant form? Maybe, in the thin cold Martian atmosphere, photochemical reactions occurred between traces of H_2O and the ultraviolet (UV) radiation from the Sun, leading to hydrogen peroxide (H_2O_2) which in turn condensed onto the soil grains. Such an H_2O_2 frost would indeed be highly oxidizing upon thawing, capable of destroying organics, as observed during the Viking missions.

Our laboratory experiments are based on a distinctly different line of thought, without the need to invoke an H_2O_2 frost. We have studied the physical and chemical properties of terrestrial magmatic minerals that crystallize in H_2O -laden magmas, and which are analogs for minerals in the Martian soil. Their surfaces become strongly oxidizing as the result of a series of solid state reactions, starting with the dissolution of H_2O during crystallization. Structurally dissolved H_2O commonly occurs as pairs of hydroxyl groups, OH^- . Many OH^- pairs undergo a redox conversion splitting them into molecular hydrogen (H_2) and peroxy (O_2^{2-}). The H_2 are mobile and diffuse out. The lattice-bound O_2^{2-} dissociate, either thermally or upon UV irradiation, generating O^- radicals. Inside the mineral structure, these O^- behave as electronic defects, similar to the "holes" known to semiconductor physics. They move as electronic charge carriers through the crystal structure. Because they carry a positive charge and repel each other in the bulk, they are pushed toward the surface. At the surface the O^- reveal their radical, highly oxidizing nature. They can strip an H atom from methane, CH_4 , the most stable of all hydrocarbons, leading to methyl radicals, $\bullet CH_3$. The reaction between surface O^- and CH_4 is of prime importance to the petrochemical industry for the conversion of methane into liquefiable hydrocarbons.

Because O^- are omnipresent in terrestrial magmatic minerals, they will also exist in the corresponding minerals on Mars. This suggests that the Mars Soil Oxidant has a similar origin, also consisting of O^- surface radicals derived from peroxy within the mineral grains.

To study O^- in natural and synthetic materials we developed a new technique called Charge Density Analysis. CDA has received the endorsement by NIST (1992) "*...as a new technique to measure previously unmeasurable fundamental properties of materials.*" It measures the dielectric polarization in an electric field gradient at the limit of 0 Hz and determines surface charges which appear or disappear during heating/cooling or after UV irradiation.

The bulk dielectric polarization (F_Σ) and surface charge contribution (F_Δ) of MgO and upper mantle derived olivine single crystals were measured as a function of temperature in the 100–600°C

interval during stepwise heating. The bulk polarization of olivine single crystals at 0.1 MPa in N₂ and CH₄-N₂ gas mixtures increases in two steps, at 150–250°C and 450–500°C. Between 400–500°C mobile charges are generated which cause the surface to become positively charged. These charge carriers bear the characteristic features of positive holes, e.g. defect electrons or O⁻ states on the O²⁻ sublattice. They are not defect electrons on the cation sublattice, e.g. Fe³⁺ resulting from the transient oxidation of Fe²⁺, for instance by traces of O₂. The O⁻ charge carriers are generated from electrically inactive precursors which may exist in the olivine structure in form of peroxy links (O₃Si/O⁻SiO₃), originating from Si-OH⁻ pairs that have undergone a redox conversion and split off an H₂ molecule. In pure N₂ the bulk polarization was reversible within ±3% up to 600°C, somewhat less upon heating to 800°C, indicating that the O⁻ charge carriers reversibly recombine. In the presence of CH₄ the bulk polarization decreased during successive heating and cooling cycles, while the surface remained positively charged. This indicates that O⁻ charge carriers are being annihilated at the crystal surface, probably by the reaction CH₄ + O⁻ = •CH₃ + OH⁻. The presence of O⁻ charge carriers has implications for the interpretation of electrical conductivity measurements of olivine under simulated upper mantle conditions, usually CO-CO₂ mixtures. The anomalously high conductivity up to 670–800°C which has always been observed during initial heating in conductivity experiments has until now been assigned to surface contamination. The CDA results suggest that this conductivity is caused by O⁻ charge carriers which are indigenous defects in the olivine crystals as delivered from the upper mantle.

Publications from Task 4:

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Task 5. CHEMIN: an XRD/XRF camera for the mineralogical analysis of Mars soil.

Science background for the instrument. CHEMIN will determine the quantitative mineralogy of an unknown material by performing X-ray diffraction (structural) and X-ray fluorescence (elemental) analysis. X-ray diffraction is distinct from all other techniques (which characterize mineralogy only indirectly), in that diffraction methods can be used to determine mineralogy directly and unequivocally without a requirement for ground truth data.

Science goal. Mineralogical analysis of Mars soil and rocks could lend insight into the early history of Martian volatiles, could establish the presence and lateral extent of hydrothermal systems, and could reveal the locations of rock types (silica sinter, travertine, clays, etc.) which might harbor evidence of liquid water, prebiotic organic material or even extinct life. Furthermore, it is probable that any robotic search for evidence of an ancient Martian biosphere will have as its focus the identification of key minerals in likely host rocks rather than the direct detection of organic or isotopic biomarkers. Even in the case of sample return, mineralogical screening will be utilized to choose the most promising candidate rocks.

Measurement objectives. The CHEMIN XRD/XRF will perform quantitative mineralogical analysis of soil or dust samples provided directly to the instrument, or of rock samples after suitable sample preparation (i.e., grinding). CHEMIN will unequivocally identify the minerals present in a complex mixture, their grain size and crystallinity, and the proportion of amorphous material present. CHEMIN will provide a complete elemental analysis of the sample material for all elements, carbon and above.

Current state-of-the-art. The instrument is in the proof-of concept stage. CCD instruments have been flown on numerous space missions, and CCDs have been fabricated which have the desired properties for use as X-ray detectors. The geometry of the instrument and the use of a CCD for both XRD and XRF is new. Significant challenges in the design of the flight instrument include the miniaturization of the X-ray source and the design of a sample preparation device for whole rock analysis. The instrument will analyze Mars soil without sample preparation.

We interfaced a camera fitted with a Tektronix TK-512X X-ray sensitive CCD to an Apple Quadra 800 computer, so that images could be recorded directly into the computer. A diffraction chamber was built which bolts directly to the CCD camera and is vacuum tight. A collimator was built in which we could vary the diameter of the entrance and exit apertures. The original collimator had an entrance aperture of 1 mm X 3 mm and an exit aperture of about 1 mm. This was ultimately replaced with an entrance aperture of 0.1 mm and a 0.03 mm exit aperture. Software was written which allowed the collection and summation of a large number of short exposures of the CCD. After each exposure, all of the photons which had the energy of a primary X-ray beam photon ($\text{CuK}\alpha$, 8.04 KeV) were summed into a 2-dimensional integer array. Over a period of a few

hours, as many as a thousand single-photon counted images could be summed to create a diffraction pattern comprised of only monochromatic $\text{CuK}\alpha$ X-rays. The software which was written to provide for the collection of single photon counted images also sums the X-rays into an energy-dispersive histogram. The histogram is comprised of XRF photons from the sample as well as Bremstrahlung (background) and characteristic radiation from the X-ray tube. This spectrum can be used to determine the elemental composition of the sample.

We have begun to quantitatively interpret the 2θ data from the diffraction patterns by Rietveld analysis. In Rietveld analysis, an unknown complex diffraction pattern is fit with various known patterns by computer matching and optimization, and residual intensities are minimized. This is the most widely used method to reduce complex XRD data, and represents an important part of our strategy of quantitative mineralogy. We have introduced sample movement into the analysis strategy to improve the quality of the patterns. There are two reasons why this is necessary: First, as the beam diameter of the instrument is decreased, less and less material contributes to the diffraction pattern. Second, in many natural materials, large crystallites result in a spotty pattern which can be improved by sampling a number of volumes of the material.

Publications from Task 5:

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Task 6: Analysis of Stratospheric Aerosols

In this task, particle collectors flown in the stratosphere and troposphere are analyzed using Scanning Electron Microscopy. During the previous two years of the research, an analytical protocol was developed and fifteen Ames wire impactors were measured for stratospheric and tropospheric soot and other aerosol sized particles. As part of the protocol, ~40 soot particles are found and imaged on each wire. The total area scanned during the particle search is used to calculate the volume swept by the wire, using the total exposure time of the wire and the speed of the ER-2 or DC-8 during the collection. Each soot particle is measured and statistics are calculated including size and shape, total volume and total mass of soot per wire. The result is a data set for Stratospheric and Tropospheric soot loading from 1991-93 covering the range 90°N latitude to 45° S latitude. Data and preliminary conclusions were presented at the Atmospheric Effects of Stratospheric Aircraft meeting in June of 1993 (Blake and Kato, 1993a), in an abstract presented at the American Geophysical Union (Blake and Kato, 1993b) and in a manuscript submitted for publication (Blake and Kato, 1994). Briefly, we found that moderately high concentrations of soot exist in the well-traveled North Atlantic flight corridor. While the soot signal in this corridor is easily detected, the total amount of soot in terms of number density, volume and surface area is less than comparable sulfuric acid aerosol loading due to the recent eruption of Mt. Pinatubo in the Philippines.

Publications from Task 6:

- Blake, D.F. and K. Kato (1993a) "Latitudinal distribution of carbon soot in the stratosphere." Annual meeting, High Speed Research Program, Virginia Beach, VA.
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- Blake, D.F. and K. Kato (1994) "Latitudinal distribution of carbon soot in the upper troposphere and lower stratosphere." JGR--Atmospheres 100, 71-95-7202 (1995).